PCT
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C09D 4/00, C08F 222/10, C03C 17/30, B65D 25/34 — A1

(11) International Publication Number: WO 98/51746

(43) International Publication Date: 19 November 1998 (19.11.98)

(21) International Application Number: PCT/EP98/02847

(22) International Filing Date: 14 May 1998 (14.05.98)

(30) Priority Data:
197 20 292.6 — 15 May 1997 (15.05.97) — DE
= DE-A-

(71) Applicant (*for all designated States except US*): PPG INDUSTRIES, INC. [US/US]; One PPG Place, Pittsburgh, PA 15272 (US).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): KRANIG, Wolfgang [DE/DE]; Erlengrund 276, D-48308 Senden (DE). MEISENBURG, Uwe [DE/DE]; Im Höschegrund 102, D-47259 Duisburg (DE). ZURSTRASSEN, Anneliese [DE/DE]; Hülsheide 13, D-48165 Münster (DE). VON WULFEN, Norbert [DE/DE]; Duesbergweg 65b, D-48153 Münster (DE).

(74) Agent: STERNAGEL & FLEISCHER; Braunsberger Feld 29, D-51429 Bergisch Gladbach (DE).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: RADIATION-CURABLE COATING MATERIAL AND ITS USE FOR PRODUCING MULTICOAT PAINT SYSTEMS, ESPECIALLY FOR COATING PACKAGING CONTAINERS

(57) Abstract

The present invention provides a radiation-curable coating material comprising at least one radiation-curable binder having at least two acrylic ester and/or methacrylic ester groups, which comprises (a) as binder (a) a mixture of (a1) at least one binder (a1) having at least two acrylic ester and/or methacrylic ester groups and having an elongation at break of at least 20 %, preferably at least 40 %, and (a2) at least one further binder (a2) which is different from (a1) and has at least two acrylic ester and/or methacrylic ester groups, (b1) at least one silicone-containing lubricant (b1) and (b2) at least one halogen-containing polyolefin wax (b2). The invention also provides for the use of this coating material for producing multicoat paint systems, especially as a clearcoat or as a topcoat, and to its use for coating glass metal substrates, especially for coating packaging containers.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

RADIATION-CURABLE COATING MATERIAL AND ITS USE FOR PRODUCING MULTICOAT PAINT SYSTEMS, ESPECIALLY FOR COATING PACKAGING CONTAINERS

The present invention relates to a radiation-curable coating material comprising at least one radiation-curable binder having at least two acrylic ester and/or methacrylic ester groups.

The invention also relates to the use of this coating material for producing multicoat paint systems, especially as a clearcoat or as a topcoat, and to its use for coating glass and metal substrates, especially for coating packaging containers.

Packaging containers (sometimes referred to just as containers below) that are employed include, in particular, glass bottles and other glass containers, and also metal containers, such as two- and three-piece beverage cans and preserve cans, for example. Such packaging containers are provided on the outside with a decorative coating. One of the functions of this coating is to protect the packaging containers against the mechanical stresses to which the packaging containers are exposed not only in the course of their production but also during the process of being filled with their contents, and during the transportation and distribution of the filled packaging containers. For instance, the packaging containers rub against one another, for example, on the conveyor belts and come into contact with the guide rails in the course of transportation. The coating materials that are employed for the exterior coating of packaging containers consisting both of glass and of metal are therefore required to have an extremely high scratch resistance in order to provide effective protection of the packaging containers from these severe mechanical stresses, for example, on the conveyor belts.

On the other hand, high lubricity is also required in the coated packaging containers, so as to ensure frictionless running in the filling installations, which run at high speed.

In the laboratory, this required lubricity of the coatings is simulated, for example, by measuring the so-called mobility of the coatings. This mobility is measured by measuring the resistance to sliding over a ballbearing. This measurement produces relative values from 0 to 0.25. The smaller the value, the better the lubricity. Mobilities of less than 0.09 are desired.

The scratch resistance is measured in the laboratory by means, for example, of a so-called Dur-O-Tester. In this case, a metal pin is pressed onto the coating by way of a spring, with a certain force, and then is guided over the coated area. The parameter measured is the spring force required to cause damage to the coated surface. The higher the values measured, the better the scratch resistance. Values of at least 7 N are desired.

In the case of packaging containers produced from metal, the applied coatings must be highly flexible as well as possessing the high scratch resistance. The reason for this is that metal packaging containers are normally produced by first of all providing metal sheets or strips (coils) with the desired coating and then processing the ready-coated strips or sheets to form the appropriate containers. In the course of the forming steps, however, there must be no damage to the coating, since otherwise the above mentioned protective function of the coatings is no longer provided.

Nowadays, on modern coating lines for metal containers, the containers pass through at very high speeds. Belt speeds of more than 100 m/min require highly reactive coating materials which in UV

applications, for example, must be able to be cured with a dose of from 200 mJ/cm^2 to 280 mJ/cm^2.

In addition to the protective function, however, the coating materials are also required to fulfill an increasingly important decorative function. For this reason, many containers coated white beforehand are printed with printing ink and then overcoated with clearcoats. The clearcoats used here are intended not only to meet the chemical resistances required, in the case, for example, of the sterilization of the filled packaging containers, but also to give outstanding brightness through well-leveling surfaces with precisely adjusted gloss. Inherent coloring or yellowing of the clearcoat must be ruled out here.

Besides metal packaging containers, descriptions have been given of providing glass bottles with plastic coatings, and in this context there has also been a description of the need to apply such plastic coatings on-line directly following the production of the glass bottles. The international patent applications WO 90/05 031 and WO 90/05 088 describe the production of transparent coatings on glass containers, which are intended to give high gloss and abrasion resistance. Before applying the transparent coatings it is possible on glass containers, as is the case with metal packaging containers, to apply inscriptions and labels, which are protected by the coatings. Coating materials used are solvent-borne, acrylic-based coating materials that can be cured by means of ultraviolet radiation. These coating materials are sprayed on, whereupon the solvent is evaporated and the coating that remains is cured by ultraviolet light.

DE-A-41 30 682 discloses the coating of glass articles with radiation-curable coating materials. It also mentions the adhesion-promoting effect of silanes. In the application process, formulations

are employed in which the low viscosity required for spraying is established by way of acrylic acid derivatives and low molecular compounds with hexanediol diacrylate and/or TMP triacylate. These substances are toxicologically objectionable and therefore undesirable.

DE-A-195 27 667.1, finally, discloses laminar materials for producing coated glass products, in which first of all a silane adhesion promoter lamina and at least one lamina of a radiation-curable coating material are applied to the glass surface and then both laminae are subjected to conjoint curing. Radiation-curable coating materials having the high flexibility required with a coating of metal containers, however, are not described in this application.

The object on which the present invention is based is therefore to provide coating materials that are suitable for the coating of both glass and metal substrates and meet the requirements commonly placed on such coating materials. In particular, the coating materials are intended to lead to coatings which combine high scratch resistance and good lubricity with high flexibility, allowing subsequent deformations of the coated substrates. The coating materials, furthermore, are intended to possess an extremely high reactivity so that they can be applied on coating lines operating at high speed.

When the coating materials are used for the coating of packaging containers the coating materials should also meet the requirements which are commonly set in this sector. In addition, the resulting coatings should possess good chemical resistance, in particular a good resistance to sterilization and to pasteurization.

This object is surprisingly achieved by a coating material of the type specified at the outset which comprises

(a) as binder (a) a mixture of

(a1) at least one binder (a1) having at least two acrylic ester and/or methacrylic ester groups and having an elongation at break of at least 20%, preferably at least 40%, and

(a2) at least one further binder (a2) which is different from (a1) and has at least two acrylic ester and/or methacrylic ester groups,

(b1) at least one silicone-containing lubricant (b1) and

(b2) at least one halogen-containing polyolefin wax (b2).

The invention also provides for the use of this coating material for producing multicoat paint systems, especially as a clearcoat or as a topcoat, and to its use for coating glass and metal substrates, especially for coating packaging containers.

It is surprising and was not foreseeable that the coating materials possess high reactivity and lead to coatings having good scratch resistance and mobility coupled with high flexibility, so that the coating materials of the invention can be employed both for coating glass containers and for coating metal sheets or metal panels that are subsequently processed to form packaging containers. A further advantage is that the resulting coatings possess good chemical resistance, and in particular good resistance to sterilization and to pasteurization. Finally, the non-aqueous coating materials of the invention feature a high nonvolatiles content, preferably a nonvolatiles content of more than 90% by weight, based on the overall weight of the coating material.

In the text below, then, the individual constituents of the coating material of the invention will first of all be elucidated further.

It is essential to the invention that the coating materials comprise at least one binder (component (a1)) having at least 2 acrylic

ester and/or methacrylic ester groups and having an elongation at break of at least 20%, preferably at least 40%.

The elongation at break here is defined as the elongation (extension) of a sample specimen (in this case, a free film) until cracks appear. This elongation is measured, for example, with the aid of the Zwick OPM 1425 tester from Zwick GmbH & Co., Ulm. The measurement is in accordance with DIN 53 457 and DIN 53 455.

The preparation of the free films used to measure the elongation at break is carried out in a manner known to the skilled worker by first of all, for example, masking off a glass plate (size 10 cm x 15 cm), or another substrate to which the coating material does not adhere, such as polypropylene or Teflon, for example, with Tesafilm (adhesive tape) strips (type 4104) and the left- and righthand edge, and applying the test binder in the form of a solution, using a doctor blade, with a wet film thickness of about 40 μm. The film is then cured by means of UV radiation using an Hg vapor lamp (irradiated energy generally 400 - 800 mJ/cm^2) and stored at 23°C for 1 day. The Tesafilm strips are then peeled off, and using, for example, a cutter blade or the like, 4 strips (1.5 cm wide and 13 - 14 cm long) are cut out. The coat thickness of the cured strips is subsequently measured with the aid of a precision dial gauge or the like. The elongation at break (elongation in % of the sample specimen until cracks occur, based on the original length) is measured, for example, with the Zwick OPM 1425 tester from Zwick GmbH & Co., Ulm at a drawing speed of 12.5 mm/min and with an initial force of 0.05 N. The value stated in each case is the average of at least 6 measurements.

Examples of compounds employed as component (a1) are polyether acrylates, polyester acrylates, epoxy acrylates, urethane acrylates and the corresponding methacrylates. The high elongation at

break required, of at least 20% and preferably at least 40%, is achieved in these binders in a manner familiar to the skilled worker through an appropriate selection of the binder's structural components.

Polyester (meth)acrylates are known to the skilled worker and can be prepared by a variety of methods. For example, acrylic acid and/or methacrylic acid can be employed directly as the acid component in the synthesis of the polyesters. Another possibility is to employ hydroxyalkyl esters of (meth)acrylic acid as the alcohol component, directly, when synthesizing the polyesters. Preferably, however, the polyester (meth)acrylates are prepared by acrylicizing polyesters. It is possible, for example, first of all to synthesize hydroxyl-containing polyesters which are then reacted with acrylic and/or methacrylic acid. It is also possible first to synthesize carboxyl-containing polyesters which are then reacted with a hydroxylalkyl ester of acrylic and/or methacrylic acid. Unreacted (meth)acrylic acid can be removed from the reaction mixture by washing, distillation or, preferably, by reaction with an equivalent amount of a mono- or diepoxide compound using appropriate catalysts, such as triphenylphosphine, for example. For further details regarding the preparation of polyester acrylates reference may be made, in particular, to DE-A-33 16 593 and DE-A-38 36 370 and also to EP-A-54 105, DE-B-20 03 579 and EP-B-2866.

Polyether (meth)acrylates are likewise known to the skilled worker. They can be prepared by a variety of methods. For example, hydroxyl-containing polyethers can be esterified with acrylic acid and/or methacrylic acid. The hydroxyl-containing polyethers can be obtained by reacting di- and/or polyhydric alcohols with various amounts of ethylene oxide and/or propylene oxide in accordance with well-known methods (cf. e.g. Houben-Weyl, Volume XIV, 2, Makromolekulare Stoffe II,

(1963)). Also employable are polymerization products of tetrahydrofuran or of butylene oxide.

Flexibilization of the polyether (meth)acrylates and of the polyester (meth)acrylates is possible, for example, by reacting corresponding OH-functional prepolymers and/or oligomers (based on polyether or polyester) with relatively long-chain, aliphatic dicarboxylic acids, especially aliphatic dicarboxylic acids having at least 6 C atoms, such as adipic acid, sebacic acid, dodecanedioic acid and/or dimeric fatty acids, for example. This flexibilization reaction can be carried out before or after the addition of acrylic and/or methacrylic acid onto the oligomers and/or prepolymers.

Furthermore, epoxy (meth)acrylates are also well known to the skilled worker and therefore need not be elucidated further. They are normally prepared by addition reaction of acrylic acid with epoxy resins, for example with epoxy resins based on bisphenol A, or with other commercially customary epoxy resins.

Flexibilization of the epoxy (meth)acrylates is possible analogously, for example, by reacting corresponding epoxy-functional prepolymers and/or oligomers with relatively long-chain, aliphatic dicarboxylic acids, especially aliphatic dicarboxylic acids having at least 6 C atoms, such as adipic acid, sebacic acid, dodecanedioic acid and/or dimeric fatty acids, for example. This flexibilization reaction can be carried out before or after the addition of acrylic and/or methacrylic acid onto the oligomers and/or prepolymers.

Urethane (meth)acrylates are likewise well known to the skilled worker. They can be obtained by reacting a di- or polyisocyanate with a chain extender from the group of the diols/polyols and/or diamines/polyamines and/or dithiols/polythiols and/or alkanolamines and then reacting the remaining free isocyanate groups with at least one

hydroxyalkyl (meth)acrylate or hydroxyalkyl ester of other ethylenically unsaturated carboxylic acids.

The amounts of chain extender, di- and/or polyisocyanate and hydroxyalkyl ester in this case are preferably chosen such that

1.) the ratio of equivalents of the NCO groups to the reactive groups of the chain extender (hydroxyl, amino and/or mercaptyl groups) lies between 3:1 and 1:2, preferably at 2:1, and

2.) the OH groups of the hydroxylalkyl esters are present in a stochiometric amount with respect to the remaining free isocyanate groups of the prepolymer formed from isocyanate and chain extender.

It is also possible to prepare the polyurethane acrylates by first reacting some of the isocyanate groups of a di- or polyisocyanate with at least one hydroxyalkyl ester and then reacting the remaining isocyanate groups with a chain extender. In this case too the amounts of chain extender, isocyanate and hydroxyalkyl ester are chosen such that the ratio of equivalents of the NCO groups to the reactive groups of the chain extender lies between 3:1 and 1:2, preferably at 2:1, and the ratio of equivalents of the remaining NCO groups to the OH groups of the hydroxylalkyl ester is 1:1. All intermediate forms of these two methods are also possible, of course. For example, some of the isocyanate groups of a diisocyanate can be reacted first of all with a diol, and then a further portion of the isocyanate groups can be reacted with the hydroxyalkyl ester and, following on from this, the remaining isocyanate groups can be reacted with a diamine.

These various preparation techniques for the polyurethane acrylates are known (cf. e.g. EP-A-204 161) and therefore require no more detailed description.

Flexibilization of the urethane (meth)acrylates is possible, for example, by reacting corresponding isocyanate-functional prepolymers and/or oligomers with relatively long-chain, aliphatic diols and/or diamines, especially aliphatic diols and/or diamines having at least 4 C atoms, such as butanediol, hexanediol and the like, and/or the corresponding amines. This flexibilization reaction can be carried out before or after the addition of acrylic and/or methacrylic acid onto the oligomers and/or prepolymers.

Examples that may be mentioned of suitable binders (a1) are also the following commercially available products:
epoxy acrylate Crodamer UVE 150 from Croda Resins Ltd., Kent, GB;
urethane acrylate Crodamer UVU 300 from Croda Resins Ltd., Kent, GB;
silicone-modified polyester acrylate Crodamer UVS 500 from Croda Resins Ltd., Kent, GB;
urethane acrylate Actilane 20/20 from Akcros Chemicals Ltd., GB;
urethane acrylate Actilane 2030 PEA from Akcros Chemicals Ltd., GB;
polyester acrylate Genomer D900 from Rahn Chemie;
polyester acrylate Genomer T1200 from Rahn Chemie;
polyester acrylate Genomer T1200 PP from Rahn Chemie;
urethane acrylate Ebecryl 210 from UCB, Drogenbos, Belgium;
urethane acrylate Ebecryl 211 from UCB, Drogenbos, Belgium;
urethane acrylate Ebecryl 230 from UCB, Drogenbos, Belgium;
urethane acrylate Ebecryl 265 from UCB, Drogenbos, Belgium;
urethane acrylate Ebecryl 270 from UCB, Drogenbos, Belgium;
poly-acrylic acrylate Ebecryl 754 from UCB, Drogenbos, Belgium;
urethane acrylate/methacrylate Ebecryl 1265 from UCB, Drogenbos, Belgium;
urethane acrylate/methacrylate Ebecryl 1259 from UCB, Drogenbos, Belgium;

urethane acrylate Ebecryl 4833 from UCB, Drogenbos, Belgium;
urethane acrylate Ebecryl 5264 from UCB, Drogenbos, Belgium.

In addition to the resins mentioned below which are used with particular preference, additional preference is given to the use of Actilane 20/20; Crodamer UVS 500; Genomer D900, T1200 and T1200PP; Ebecryl 265, 270, 754, 5264 and 5284, and particular preference is given to the use of Crodamer UVE 150 and UVU 300; actilane 2030PEA and Ebecryl 210, 211, 1259 and 4833.

The binder (a1) is employed in the coating materials of the invention preferably in an amount of from 2.5 to 80, with particular preference from 10 to 50% by weight, based on the overall weight of the coating material.

It is assumed that the addition of the binder (a1) contributes, on the one hand, to avoiding instances of flaking when the coatings are subjected to mechanical stress and, on the other hand, especially when relatively large amounts of preferably at least 10% by weight, based on the overall weight of the coating material, are used, contributes to the desired deformability of the coatings (can manufacture).

As a further binder component (a2) the coating materials of the invention comprise preferably also from 19.8 to 97.3% by weight, with particular preference also from 25 to 89.8% by weight, based on the overall weight of the coating material, of at least one further binder which is different from component (a1) and has at least 2 acrylic ester and/or methacrylic ester groups.

If the coating materials are employed for the coating of substrates where no great requirements are placed on the flexibility of the resulting coatings, but instead the abrasion resistance/scratch resistance of the coatings is particularly important, as in the case of

the coating of glass bottles, for example, then the binder (a1) is employed preferably in very small amounts and, with particular preference, in amounts of from 2.5 to 15% by weight, based on the overall weight of the coating material. In this case the binder (a2) is employed with particular preference in an amount of from 40 to 95% by weight, based on the overall weight of the coating material.

If the coating materials are used, on the other hand, to coat substrates where very high requirements are placed on the flexibility of the resulting coatings, as in the case, for example, of the coating of metal packaging containers, then the binder (a1) is preferably employed in very large amounts and, with particular preference, in amounts of from 10 to 50% by weight, based on the overall weight of the coating material. In this case the binder (a2) is employed with particular preference in an amount of from 40 to 80% by weight, based on the overall weight of the coating material. This coating material can of course also be employed with a high proportion of (a1) for the coating of substrates which are less demanding in terms of flexibility, such as glass bottles, for example.

As component (a2) it is possible, for example, to employ the amino-containing binders described in the international patent application WO 93/21240 on page 5, line 21, to page 10, line 18, and also further amine-modified binders, such as, for example, the binders known from EP-A-280 222, those known from US-A-4,045,416, from US-A-4,547,562 and from US-A-4,675,374.

Furthermore, other binders that are commonly employed in radiation-curable coating materials and have (meth)acrylate groups can also be employed. For instance, examples of compounds suitable as component (a2) are polyether acrylates, epoxy acrylates, polyester acrylates, urethane acrylates and the corresponding methacrylates. These

binders (a2) have a lower elongation at break than the binders employed as component (a1). The binders (a2) therefore generally possess an elongation at break of less than 20%, preferably less than 10% and, with particular preference, less than 5%.

Examples that may be mentioned of suitable components (a2) are the following binders: polyether acrylates, e.g. Laromer P083 F, P084 F, P085 F and Laromer LR 8863 from BASF AG, Viaktin VTE 5978 from Hoechst, Sartomer 494 from Harcros, epoxy acrylates, for example Laromer LR 8765 from BASF AG, UVE 140 from Croda Resins, or polyester acrylates, for example Laromer LR 8799 and Laromer LR PE 55 W from BASF AG, Viaktin VTE 5970 from Hoechst and Setacure EPS 2553 from Akzo-Nobel, and also urethane acrylates, e.g. Viaktin 5960 and Viaktin VTE 1420 from Hoechst, and Ebecryl 264 and 284 from UCB.

If desired it is also possible to employ oligomeric, ethylenically unsaturated compounds, such as tripropylene glycol diacrylate, dipropylene glycol diacrylate, hexanediol diacrylate and the like, for example.

It is assumed that the addition of the binder (a2) leads to an improvement in the scratch resistance (avoidance of damage to the coating under mechanical stress on conveyor belts and the like), which only with the addition of lubricants (components (b1) and (b2)) would not be achievable to the same extent without causing other disadvantages.

It is also essential to the invention that the coating materials additionally comprise at least one silicone-containing lubricant (b1), preferably in an amount of 0.1 to 3% by weight, with particular preference from 0.2 to 2% by weight, based in each case on the overall weight of the coating material.

All commonly employed silicone-containing lubricants are suitable as component (b1). Preference, however, is given to the use of polyether-modified, silicone-containing lubricants. These silicone-containing lubricants are known in principle to the skilled worker and need therefore not be elucidated further. They are also obtainable commercially in large numbers.

Examples of suitable compounds that may be mentioned are the products obtainable commercially under the name Byk® 301, 306, 307 and 333 from Byk-Chemie GmbH, Wesel.

In addition, the coating materials of the invention also include at least one halogen-containing polyolefin wax (component (b2)) as a further lubricant which is different from component (b1), and preferably in an amount of from 0.1 to 5% by weight, with particular preference from 0.2 to 3% by weight, based in each case on the solids content of (b2) and on the overall weight of the coating material.

The use of component (b2) is particularly advantageous with coating materials that are employed in the field of the coating of packaging containers, with respect, for example, to the abrasion resistance of the resulting coatings. Surprisingly, such waxes also increase considerably the reactivity of the coating materials.

As component (b2) it is possible to employ all commonly employed halogen-containing polyolefin waxes, examples being halo-substituted polyethylene and/or polypropylene waxes, especially polytetrafluoroethylene waxes. Preference is given to the use of fluorine-substituted polyolefin waxes, especially polyfluoro waxes.

Examples of suitable waxes are also the products obtainable commercially under the following names:

Polyfluoro waxes, such as "Polyfluo 190, 400, 540 and 635 VF" from Micro Powders, Inc., New York;

"Cerafluor grades", such as Cerafluor 900, 910 and 930 from Byk Chemie

The coating materials of the invention preferably include as well at least one further lubricant (component (b3)) that is different from components (b1) and (b2). As component (b3) it is preferred to employ halogen-free waxes, examples being polyethylene and/or polypropylene waxes, ester-based waxes, and the like. Other organic lubricants, however, can also be employed as component (b3).

Examples of suitable polyolefin waxes (b3) are also the products obtainable commercially under the following names:
"Ceramat grades", such as e.g. Ceramat 250 from Byk Chemie
"Cerafac grades", such as e.g. Cerafac 59 from Byk.

Particular preference is given in the coating materials of the invention to the use of a mixture of a polyfluoro wax (commercial product Polyfluo 540 from Micro Powders) and a polyolefin wax (commercial product Cerafac 59 from Byk).

Component (b3) is preferably employed in an amount of from 0.1 to 3% by weight, with particular preference from 0.2 to 2% by weight, based in each case on the solids content of (b3) and on the overall weight of the coating material.

The binder mixture additionally comprises, if desired, up to 5% by weight, preferably from 0.5 to 2.5% by weight, based on the overall weight of the coating material, of at least one silane (component (c)).

In accordance with the invention it is preferred to employ a low molecular mass silane. Particularly suitable silanes are those having ethylenically unsaturated groups, or condensation products thereof.

Examples of such compounds are $CH_2{=}C(CH_3)\text{-}COO\text{-}(CH_2)_3\text{-}Si(OCH_3)_3$, $CH_2{=}CH\text{-}Si(OCH_3)_3$, $CH_2{=}CH\text{-}Si(OC_2H_5)_3$, $CH_2{=}CH\text{-}Si(OC_2H_4\text{-}OCH_3)_3$.

The coating materials of the invention optionally include as component (d) in proportions of from 0 to 6% by weight, preferably in UV-cured formulations, preferably from 2 to 5% by weight, based on the overall weight of coating composition, of customary photoinitiators that are employed in radiation-curable coating materials, examples being benzophenones, benzoins or benzoin ethers. It is also possible, for example, to employ those in commerce under the names Irgacure® 184, Irgacure® 1800 and Irgacure® 500 from Ciba Geigy and Genocure® MBF from Rahn.

When selecting appropriate photoinitiators account should be taken of the different curing mechanisms. Thus photoinitiators based on benzophenone and based on benzophenone derivatives generally require amines as synergists, whereas these very amines inhibit other photoinitiators, such as, for example, the photoinitiator obtainable commercially under the name Genocure MBF.

The fillers and/or pigments (e) that may be present, if desired, in the coating compositions of the invention in amounts of up to 15% by weight, based on the overall weight of the coating material, can be inorganic and/or organic materials.

As exemplary of inorganic fillers and/or pigments there may be mentioned: titanium dioxides, sulfates, such as barium sulfates (heavy spar) or potassium sulfates (light spar), for example, or silicates, such as kaolins, mica or quartz flour, for example. In the case of the inorganic fillers and/or pigments (e) it should be borne in mind that the conceptual distinction between "filler" and "pigment" is often possible only with difficulty, since substances such as barium sulfate or titanium dioxide, for example, function simultaneously as filler and pigment.

By way of example of organic fillers and/or pigments and as representative of many there may be mentioned: carbon blacks, azo dye pigments, or phthalocyanine dye pigments.

Continuing, the coating materials of the invention may also comprise customary auxiliaries and/or additives (f), examples of which are defoamers, leveling agents, light stabilizers and film-forming auxiliaries, e.g. cellulose derivatives. These customary auxiliaries and/or additives are commonly employed in an amount of up to 15% by weight, based on the overall weight of the coating material.

In accordance with the invention it is preferred to employ monomer-free or low-monomer coating materials. The coating materials (non-aqueous) therefore preferably contain a nonvolatile fraction of more than 90% by weight (monomer fraction preferably < 10%).

Depending on the viscosity of the binders that are employed in accordance with the invention the coating materials can, if desired, include relatively small amounts, preferably from 0 to 4% by weight, based on the overall weight of the coating material, of organic solvents (component (g)) in addition.

Finally, depending on the viscosity of the binders that are employed in accordance with the invention, the coating materials of the invention may also include water.

DE-A-195 45 125.2, which is not a prior publication, describes a process by which radiation-curable coating compositions can be transferred to the aqueous phase. This process can also be employed for the coating materials of the invention. The process comprises the following successive steps:

1. taking a preformulated, water-incompatible precoating material A) and adding from 0.2 to 5% by weight, preferably from 1 to 3% by weight, based on the precoating material A), of a di- and/or

polyamine B) having at least one primary and at least one tertiary amino group,

2. neutralizing the amino groups of component B) with an acid, and
3. transferring the water-soluble coating material prepared in steps 1 and 2 to the aqueous phase and establishing the desired application viscosity by adding water.

In a further embodiment, the water-incompatible precoating material A) is formulated in the 1st stage of this process with the simultaneous addition of from 0.2 to 5% by weight, preferably from 1 to 3% by weight, based on the precoating material A), of component B).

In a preferred embodiment of the process the neutralization of the amino groups (step 2) and the establishment of the desired application viscosity (step 3) take place in one step using a dilute aqueous acid.

Preferred di- and/or polyamines B) are diamines having a primary and tertiary amino group.

In step 1 of the process for preparing the aqueous coating materials, component B) is added to the preformulated water-incompatible coating material A) in the liquid phase with stirring and preferably at room temperature. In the course of this addition the temperature may rise to about 40 degrees C. By raising the temperature it is possible to accelerate the incorporation of the component B). For the sake of reproducibility the incorporation should be allowed to proceed as far as possible to completion, which at temperatures above 40 degrees C is achieved within a few hours. The viscosity of the resulting mixture of A) and B) is then constant over time.

The reaction is generally conducted without solvents, although it is also possible to employ solvents, especially in order to

add solid di- and/or polyamines B) in the form of solutions. The solvent can then be removed after Michael addition has taken place.

In the 2nd step of the process, the mixture of components A) and B) that was prepared in the 1st step is converted to a water-thinnable form by neutralization, especially of the tertiary amino groups, with at least one acid and with stirring, preferably at room temperature. The acid is preferably employed in the form of its aqueous solution.

Examples of acids suitable for neutralizing the basic groups are organic acids, such as lactic acid, acetic acid or formic acid, or mineral acids, such as phosphoric acid or, preferably, hydrochloric acid.

The 3rd step of the process comprises the transfer of the water-soluble coating material prepared in steps 1 and 2 to the aqueous phase and the establishment of the desired application viscosity with water and with stirring, preferably at room temperature.

The application viscosities that are to be established in the resulting aqueous radiation-curable coating materials are generally dependent on the particular application. For instance, low viscosities for sprayable coating materials can be implemented, as can the higher viscosities required for roller application of the coating material. The water content of the coating materials of the invention in this case, depending on the viscosity to be established, normally lies at between 5 and 50% by weight, based on the overall weight of the coating material.

The coating materials of the invention can be applied to glass and to a very wide variety of metal substrates, such as aluminum, steel, various ferrous alloys, and the like, for example. In addition, they can also be used, for example, as a clearcoat or a topcoat in the field of automotive finishing. As well as their application to a wide

variety of metals the coating materials can of course also be applied to other substrates, such as wood, paper, plastics or the like, for example.

The coating materials of the invention are preferably employed in the coating of packaging containers, such as glass bottles, other glass containers and metal containers, for example, such as two- and three-piece beverage cans and preserve cans, for example. The metal sheets or metal panels or metal strips used to produce the metal containers can consist of a very wide variety of materials, such as aluminum, black plate, tinplate and various ferrous alloys, for example, which may have been coated with a wide variety of coating materials.

The packaging containers coated in this way can be employed for a very wide variety of end uses, such as, for example, for the packaging of foods and drinks, such as for beer, juices, carbonated beverages, still wine, sparkling wine, soups, vegetables, meat dishes, fish dishes, and also animal food and the like. Alternatively, they can be employed for industrial products.

To produce coatings on metal substrates the coating materials of the invention are preferably applied to metal strips or metal sheets that have been primed or coated with a basecoat. Primers which can be used are the commonly employed primers. Basecoats employed include both conventional and aqueous basecoats.

For example, primers based on epoxy resin and phenolic resin, on polyester or on polyacrylate are employed.

Other examples of suitable primers are the customary commercial white coatings for containers and the customary commercial primers for packaging containers, and also the customary commercial primers for the coating of metal panels or metal strips (known as coil coatings), such as the panel coating primer EG 030823 and the coil

coating primer EG 03060D from BASF Coatings AG, Münster. However, it is also possible to employ, for example, radiation-curable primers or the like.

Suitable basecoats are the conventional and aqueous basecoats that are commonly employed, based, for example, on polyurethanes, polyacrylates and polyester/cellulose acetobutyrates..

Where the coating materials are applied to glass, it is possible to apply a coat of an adhesion promoter, especially one based on a silane, as is described, for example, in DE-A-195 27 667, for example, before applying the coating material of the invention.

Prior to the application of the silane the substrate is heated, in a preferred embodiment of the invention. The temperatures are from 80 to 120°C, preferably about 80°C.

Mixtures of water and silane are particularly suitable for applying the silane coat. The silane content is from 0.2 to 4% by weight, preferably from 0.5 to 2% by weight. To prepare this mixture the silane is stirred at room temperature with fully deionized water and homogenized for a period, preferably about 30 minutes, with vigorous stirring.

This solution is atomized in ultrafine droplet size at elevated pressure, preferably at from 2 to 6 bar and in particular from 3 to 4 bar. The spray mist should be applied almost aerosollike in fan formation to the article that is to be coated.

In addition to this form of application it is of course also possible to use all other common application techniques; for example, knife coating, brushing, rolling, flow coating. Application from an aerosol solution, however, has been found particularly appropriate since in this case the preferred low coat thicknesses can be achieved. These lie between 0.2 and 4 μm, preferably between 1.5 and 2 μm.

As soon as the silane has been applied, the evaporation of water begins. This operation can be accelerated by the action of heat. After the evaporation procedure has been concluded, what remains is the water-free silane coat.

The use of a silane of low molecular mass is preferred. Particularly suitable silanes are those having ethylenically unsaturated groups, or condensation products thereof.

Examples of such compounds are $CH_2=C(CH_3)\text{-}COO\text{-}(CH_2)_3\text{-}Si(OCH_3)_3$, $CH_2=CH\text{-}Si(OCH_3)_3$, $CH_2=CH\text{-}Si(OC_2H_5)_3$, $CH_2=CH\text{-}Si(OC_2H_4\text{-}OCH_3)_3$.

A feature of such silanes is that they can be hydrolyzed. For the purposes of the invention it has been found that these products apply surprisingly well to smooth surfaces of glass or metal, for example.

Preferably, the product is not prepared, judiciously as a mixture with water, until shortly before its application. Immediately after mixing with water, the hydrolysis process sets in. However, there is no harm in the product being stored in water for up to 14 days; the number of oligomers formed within this period do not impair the product.

Following the application of the silane coat, the coating material of the invention is applied.

The coating materials of the invention can in principle be applied by all currently known methods; for example, by spraying, rolling, flow coating, dipping, knife coating, brushing, casting or by Vacumat application.

The curing of the coating films takes place directly following application or following the evaporation of the water present, by means of UV or electron beams. The apparatus and conditions for these curing methods are known from the literature (cf. e.g. R. Holmes, U.V. and E.B. Curing Formulations for Printing Inks, Coatings and Paints,

SITA Technology, Academic Press, London, United Kingdom 1984, pp. 79 to 111) and require no further description.

In the text below the invention is illustrated by means of working examples. All parts and percentages therein are by weight unless expressly stated otherwise.

Example 1

1.1. Preparing the coating material 1

Coating material 1 is prepared from the following components with intensive stirring by means of a dissolver or a stirrer:

21.00 parts	Crodamer® UVE 150, commercial epoxy acrylate from Croda Resins, having on average 2 acrylate groups per molecule and an elongation at break (Zwick) of about 60%, 80% strength in tripropylene glycol diacrylate
21.00 parts	Crodamer® UVP 210, commercial polyester acrylate from Croda Resins having an elongation at break of < 10%
20.00 parts	polyether acrylate 1 having an elongation at break of < 5%, prepared from ethoxylated pentaerythritol (Polyol PP 150 from Perstorp) and acrylic acid
15.20 parts	polyether acrylate 2, commercial polyether acrylate Sartomer 494 from Cray Valley having an elongation at break of < 5%
5.00 parts	tripropylene glycol diacrylate
2.00 parts	commercial silane of the formula $CH_2{=}C(CH_3)\text{-}COO\text{-}(CH_2)_3\text{-}Si(OCH_3)_3$
0.50 parts	acrylic acid
0.50 parts	wax Polyfluo 540, commercial polyfluoro wax from Micro Powders

3.00 parts	polyolefin wax dispersion, Cerafac 59 from Byk
1.00 parts	Byk® 333, commercial lubricant based on polyether-modified dimethyl polysiloxane, from Byk
3.25 parts	commercial photoinitiator Genocure MBF from Rahn
2.00 parts	methoxypropanol
0.05 parts	commercial optical brightener Uvitex OB from Ciba Geigy

The composition of the coating material 1 is summarized in Table 1.

1.2. Preparing and testing the coating 1

The coating material 1 is applied (wet film thickness 18 micrometers) to tinplate that has been coated with a commercial white coating based on polyacrylates or polyesters. Curing takes place with an 80 watt Hg UV lamp. The irradiated dose is 300 mJ/cm^2. The resulting coating was subjected to various tests. The results are summarized in Table 2. These tests were conducted as follows:

Viscosity:

The viscosity stated is that at 23°C as the flowtime from the DIN 4 cup.

Leveling and yellowing:

The leveling and yellowing are determined visually: score 1 = very good; score 5 = inadequate

Reactivity:

In order to realize the high unit counts required in the coating of the respective packaging containers, quick curing coating

materials are necessary. In this context, sufficient reactivities are indicated by small doses of UV radiation for curing. Reactivity is sufficient when the irradiated dose is not more than from 200 up to a maximum of 280 mJ/cm^2, measured in each case with a Lightbag IL 390 A from International Light INC. The respective coating is sufficiently cured at the respective dose when a fingernail scratch test is unable to cause any surface damage.

Mobility:

The mobility is measured by measuring the resistance to sliding over a ballbearing with the aid of the ALTEK instrument 9505A from ALTEK using a 2 kg weight. In this test, relative values from 0 to 0.25 are measured. The smaller the value, the better the lubricity. Mobilities of less than 0.09 are desired.

Scratch resistance:

The measurement of scratch resistance is carried out with the Dur-O-Tester from Byk-Gardner. In this test a metal pin is pressed onto the coating with a defined force, by way of a spring, and then is guided over the coated area. The measurement made is that of the spring force required to cause damage to the coated surface. The higher these measurements, the better the scratch resistance. Values of at least 7 N are desired.

Sterilization resistance:

The sterilization resistance was determined by sterilizing the coated metal panel at 120°C for 30 minutes with a 0.1% strength solution of Na_2CO_3. Subsequently, Tesafilm tear-off and water absorption are tested.

Flexibility:

The flexibility is assessed (test in accordance with the T-bend test) by bending a coated metal panel and assessing it visually for cracks at the bend: score 1 = very good; score 5 = inadequate

Examples 2 and 3

The coating materials 2 and 3 are prepared by means of a stirrer or dissolver from the components indicated in Table 1 by the method of Example 1.

Application and curing of the coating materials 2 and 3 takes place by the method of Example 1. Testing of the resulting coatings is likewise by the method of Example 1. The test results are set out in Table 2.

Comparative examples 1 to 5

The coating materials V1 to V5 are prepared by means of a stirrer or dissolver from the components indicated in Table 1 by the method of Example 1.

Application and curing of the coating materials V1 to V5 takes place by the method of Example 1. Testing of the resulting coatings is likewise by the method of Example 1. The test results are set out in Table 2.

Table 1: Compositions of the coating materials, in parts

	Ex1	V1	V2	V3	V4	V5	Ex2	Ex3
UVE150[1)]	21	77.2	-	21	21	21	21	21
UVP210[2)]	21	-	-	21	21	21	21	21
PEA 1 [3)]	20	-	-	20	20	20	20	20
PEA 2 [4)]	15.2	-	77.2	15.2	15.2	15.2	15.2	15.2
TPGDA [5)]	5	5	5	5	5	5	5	5
Sil. [6)]	2	2	2	2	2	2	2	-
Aa [7)]	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Ini.	3.25	3.25	3.25	3.25	3.25	3.25	3.25	3.25
F-wax [9)]	0.5	0.5	0.5	0.5	-	-	0.5	0.5
Wax 2 [10)]	3	3	3	3	-	3	-	3
Lubr. [11)]	1	1	1	-	1	1	1	1
MP [12)]	2	2	2	2	2	2	2	2
Add. [13)]	0.05	-	-	-	-	-	-	-
Total	94.5	94.45	94.45	93.45	90.95	93.95	91.45	92.45

Table 2: Test results

	Ex1	V1	V2	V3	V4	V5	Ex2	Ex3
Viscos. 1)	85	177	27	86	106	107	111	92
Lev. 2)	2	3	1	2	2	2	2	3
React. 3)	204	735	205	270	733	680	280	270
Mobil. 4)	0.04	0.07	0.04	0.195	0.04	0.04	0.04	0.08
Scratch 5)	10	14	7	9	8	10	10	7
Flex. 6)	2	1	4	2	2	2	2	2
Yel. 7)	1	2	2	2	2	2	2	2
Steril. 8)	sat.	sat.	Sat.	sat.	sat.	sat.	sat.	Sat.

Key to Table 1:

UVE 150:	epoxy acrylate Crodamer® UVE 150 described in Example 1
UVP 210:	polyester acrylate Crodamer® UVP 210 described in Example 1
PEA 1:	polyether acrylate 1 described in Example 1
PEA 2:	polyether acrylate 2 described in Example 1 (Sartomer® 494)
TPGDA	tripropylene glycol diacrylate
Sil.	silane described in Example 1
Aa	acrylic acid
Init.	commercial photoinitiator Genocure MBF from Rahn
F-wax	polyfluoro wax described in Example 1
Wax 2	polyolefin wax dispersion described in Example 1
Lub.	lubricant described in Example 1, based on polyether-modified dimethylpolysiloxane
MP	methoxypropanol
Add.	commercial optical brightener described in Example 1

Key to Table 2:

Viscos.:	measured as the flow time from the DIN 4 cup
Lev.:	leveling, assessed visually
React.:	radiation dose required for sufficient curing
Mobil.:	mobility, measured with the ALTEK tester
Scratch:	scratch resistance, measured in N using the Dur-O-Tester
Flex.:	flexibility, visual assessment of the appearance of cracks after bending the coated metal panel (see above)
Yel.:	yellowing, assessed visually
Steril.:	sterilization resistance: sat.: = satisfactory

Summary of the test results:

The coating materials of Examples 1 to 3 meet all of the requirements placed on them, with the coating material of Example 1 having a reactivity that is improved further in comparison to the coating materials of Examples 2 and 3, and also having a mobility and scratch resistance that is improved further in comparison to the coating material of Example 3.

The coating material of Comparative Example V1 possesses, in particular, inadequate reactivity and poor leveling. The coating material of Comparative Example V2 is, in particular, inadequate in its flexibility. The coating material of Comparative Example V3 features, in particular, inadequate mobility. The coating materials of Comparative Examples V4 and V5 are inadequate in their reactivity.

Claims:

1. A radiation-curable coating material comprising at least one radiation-curable binder having at least two acrylic ester and/or methacrylic ester groups, which comprises

(a) as binder (a) a mixture of

(a1) at least one binder (a1) having at least two acrylic ester and/or methacrylic ester groups and having an elongation at break of at least 20% and

(a2) at least one further binder (a2) which is different from (a1) and has at least two acrylic ester and/or methacrylic ester groups,

(b1) at least one silicone-containing lubricant and

(b2) at least one halogen-containing polyolefin wax.

2. The coating material as claimed in claim 1, which comprises as component (a1) at least one binder having an elongation at break of at least 40%.

3. The coating material as claimed in claim 1 or 2, which comprises

(a1) from 2.5 to 80% by weight, preferably from 10 to 50% by weight, of at least one binder (a1) and

(a2) from 19.8 to 97.3% by weight, preferably from 25 to 89.8% by weight, of at least one binder (a2),

the percentages by weight being based on the overall weight of the coating material.

4. The coating material as claimed in one of claims 1 to 3, which comprises at least one further, organic lubricant which is different from components (b1) and (b2).

5. The coating material as claimed in one of claims 1 to 4, which comprises
(b1) from 0.1 to 3% by weight, preferably from 0.2 to 2% by weight, based on the overall weight of the coating material, of at least one silicone-containing lubricant (b1) and
(b2) from 0.1 to 5% by weight, preferably from 0.2 to 3% by weight, based on the overall weight of the coating material, and at least one halogen-containing polyolefin wax (b2).

6. The coating material as claimed in one of claims 1 to 5, which comprises up to 5% by weight, preferably from 0.5 to 2.5% by weight, based on the overall weight of the coating material, of at least one silane (c), preferably at least one silane having ethylenically unsaturated groups.

7. The coating material as claimed in one of claims 1 to 6, which comprises at least one silane selected from $CH_2=C(CH_3)-COO-(CH_2)_3-Si(OCH_3)_3$, $CH_2=CH-Si(OCH_3)_3$, $CH_2=CH-Si(OC_2H_5)_3$, and/or $CH_2=CH-Si(OC_2H_4-OCH_3)_3$.

8. The use of the coating material as claimed in one of claims 1 to 7 for producing a multicoat paint system, especially as a clearcoat or as a topcoat.

9. The use of the coating material as claimed in one of claims 1 to 7 for coating metal substrates.

10. The use of the coating material as claimed in one of claims 1 to 7 for coating packaging containers, especially glass containers and/or metal containers, preferably two- or three-piece cans.